

Maybe same DECENT ART
in HZ for STABILITY? - US 5691392
is NOT very
GOOD

AN 701121 ~~EUROPATEFULL~~ JP 19970408 EW 199611 FS OS STA R
TIEN METHOD OF EVALUATING SILOXANE USED FOR FORMING INSULATION COATING,
COATING FLUID USED FOR FORMING INSULATION COATING, PROCESS FOR
PRODUCING
THE FLUID, PROCESS FOR FORMING INSULATION COATING FOR SEMICONDUCTOR
DEVICE, AND PROCESS FOR PRODUCING SEMICONDUCTOR DEVICE BY APPLYING THE
ABOVE PROCESS.
TIDE VERFAHREN ZUR BEWERTUNG DER ZUR ERZEUGUNG VON ISOLATIONSBSCHICHTUNG
VERWENDETEN SILOXANE, BESCHICHTUNGSFLUESSIGKEIT VERWENDET ZUR ERZEUGUNG
DER ISOLATIONSBSCHICHTUNG, VERFAHREN ZUR HERSTELLUNG DER FLUESSIGKEIT,
VERFAHREN ZUR HERSTELLUNG DER ISOLATIONSBSCHICHTUNG FUER
HALBLEITERBAUELEMENTE UND VERFAHREN ZUR HERSTELLUNG VON
HALBLEITERBAUELEMENTEN DURCH DIE ANWENDUNG VON OBIGEN VERFAHREN.
TIFR PROCEDE D'EVALUATION DU SILOXANE UTILISE POUR FORMER UNE COUCHE
ISOLANTE, FLUIDE D'ENROBAGE UTILISE POUR FORMER UNE TELLE COUCHE,
PROCEDE DE PRODUCTION DE CE FLUIDE, PROCEDE DE FORMATION D'UNE COUCHE
ISOLANTE POUR UN DISPOSITIF A SEMI-CONDUCTEUR, ET PROCEDE DE PRODUCTION
D'UN DISPOSITIF A SEMI-CONDU.
IN NAKANO, Tadashi, Kawasaki Steel Corp. High-Techn., Research
Laboratories
1-Banchi, Kawasaki-cho., Chuo-cho, Chuo-ku, Chiba-shi, Chiba 260, JP;
SHIMURA, Makoto, Kawasaki Steel Corporation Iron, & Steel Research
Laboratories, 1-Banchi, Kawasaki-, cho, Chuo-ku, Chiba-shi, Chiba 260,
JP;
OHTA, Tomohiro, Kawasaki Steel Corporation High-, Technology Research
Laboratories 1-Banchi Kawasaki, -cho Chuo-ku, Chiba-shi Chiba 260, JP
PA KAWASAKI STEEL CORPORATION, 1-28, Kitahonmachidori 1-chome, Chuo-ku,
Kobe-shi, Hyogo 651, JP
PAN 273194
AG Overbury, Richard Douglas, Haseltine Lake & Co Hazlitt House 28,
Southampton Buildings Chancery Lane, London WC2A 1AT, GB
AGN 34573
OS ESP1996014 EP 0701121 A1 960313
SO Wila-EPZ-1996-H11-T2a
DT Patent
LA Anmeldung in Japanisch; Veroeffentlichung in Englisch;
Verfahren in Englisch
DS R BE; R DE; R FR; R GB
PIT EPA1 EUROPAEISCHE PATENTANMELDUNG (Internationale Anmeldung)
PI EP 701121 A1 19960313
OD 19960313
AI EP 1995-900290 19941111
PRAI JP 1994-41314 19940311
RLI WO 94-JP1910 941111 INTAKZ
WO 9524639 950914 INTPNR
DETDEN. . . of semiconductor devices, a method for relieving the unevenness
of a substrate by forming an insulating film according to the
SPIN ON GLASS (SOG) method as disclosed in,
for instance, OYO BUTSURI (Applied Physics), Vol. 57, No. 12 (1988).
For instance, a hard film comprising SiO.sub2. formed by the SOG
method has generally been used as an interlayer insulating film for LSI
multilevel interconnections.
The term "SOG" means a technique comprising applying a
solution containing oligosilanols or oligosilicates to a substrate by a
spincoater and then thermally. . . of SiO.sub2., or an insulating
film formed by the method, or a coating liquid for forming an
insulating

film. The **SOG** coating solution may run into narrow grooves formed between distributing wires and the film thus formed may correspondingly fill up. . . and flat recesses. Therefore, the coating solution also permits leveling of the surface having relatively wide and high steps. The **SOG** process is performed at a low temperature on the order of about 400 .degree.C and therefore, it can be recommended. . .

There have conventionally been used, as materials for **SOG**, an oligosilicate called inorganic **SOG** represented by the general formula: $\text{Si}(\text{OR})_{\text{subn}}(\text{OH})_{\text{sub}4-\text{n}}$ and completely free of organic groups bonded to Si atoms. The inorganic **SOG** undergoes volume shrinkage at a rate of about 20% during hardening with heating. Accordingly, the resulting film has a poor resistance to crack and the inorganic **SOG** can be coated in a thickness ranging from only 200 to 300 nm by a single coating operation. An **SOG** film having a thickness at least equal to the height of distributing wires is required for relieving the steps formed by distributing wires whose cross section has an aspect ratio greater than about 1, but such a thick **SOG** film cannot be formed because the inorganic **SOG** may cause cracking. In other words, the inorganic **SOG** cannot be used for leveling a stepped pattern having a high cross sectional aspect ratio.

To eliminate the foregoing drawbacks associated with the inorganic **SOG** and to improve the shrink properties, flatness, adhesion and resistance to cracks of a film as well as the etch rate thereof, there has been investigated and developed an oligosiloxane called organic **SOG** which comprises, in the chemical structure, organic substituents directly bonded to an Si atom, i.e., an organic Si and which. . . but other kinds of substituents such as a phenyl group may sometimes be used as the organic substituent. The organic **SOG** is characterized in that the film thereof has a low shrinkage factor during hardening with heating as compared with the film of the inorganic **SOG** and therefore, the film has high resistance to cracks. In addition, the rate of etching the film with a CHF_3 -containing etching gas is low and almost comparable to that of the CVD film. Therefore, the organic **SOG** permits the use of a leveling process by the equal velocity etch back method which comprises applying a thick organic **SOG** layer on a CVD oxide film formed on a pattern, then hardening the organic **SOG** layer and etching the hardened **SOG** layer with a CHF_3 -containing etching gas simultaneously with the CVD film.

However, the hardening of the **SOG** layer by heating is initiated at about 100 .degree.C and this is accompanied by the volume shrinkage of the **SOG** layer. Thus, the surface which is once flatened by the application of the organic **SOG** ultimately has unevenness corresponding to the shape of the surface of a substrate and the flatness of the surface is. . .


Moreover, . . . above, the thickness of the film formed varies depending on the density of the wiring pattern and therefore, the organic **SOG** is useless for leveling a wide area comparable to those of chips and wafers.

Moreover, the organic **SOG** undergoes volume shrinkage on the order of at least about 7% during hardening with heating and may crack due to. . . if a film thereof having a thickness of not less than 500 nm is formed by coating, like the inorganic **SOG**.

The organic **SOG** film is inferior in the quality and liable to retain or absorb water. For this reason, various troubles are liable to arise due to the gas generated from the **SOG** film in the

subsequent processes. Moreover, the organic **SOG** film suffers from various problems such that the apparent dielectric constant thereof

increases due to the presence of water, the. . .

There has been reported several kinds of **SOG's** which can eliminate the foregoing drawbacks associated with the organic **SOG**. One of them is a ladder siloxane oligomer which can be represented by the following structural formula:  In other. .

As another measure, there has been known an inorganic **SOG** prepared from hydrogensiloxane oligomer or perhydrosilazane oligomer. These novel **SOG's** have a structure free of organic groups directly bonded to Si atoms and are, instead, characterized by having hydrogen atoms. . . substrate surface is traced on the films thereof due to the shrinkage during application and drying thereof, like the organic **SOG** and therefore, they cannot be used for leveling the surface over a wide area. Furthermore, free hydroxyl groups remain in. . .

Although. . . has not yet been established any industrially effective method for determining the proportions of organic

substituents

present in the organic **SOG** and, in particular, any industrially useful method for accurately and simply analyzing and evaluating the organic **SOG**, i.e., siloxanes for forming insulating films while correlating the results with the characteristic properties of insulating films for semiconductor devices,. . .

The. . . of the present invention is to provide a method comprising analyzing the rates of organic substituents present in an organic **SOG**, and determining the rates of Si atoms bonded to different numbers of organic groups, i.e., structural units present in the

organic

SOG or siloxanes for forming an insulating film for semiconductor devices; and evaluating the siloxanes for forming insulating films on the. . .

The. . . different numbers of organic groups bonded thereto, i.e., the rates of structural units of the siloxanes present in the organic **SOG** and that, as a result of intensive studies, the organicity of **SOG** can be evaluated on the basis of the integrated values of ²⁹Si-NMR spectral signals and that an insulating film having excellent film characteristic properties can be obtained by the use of a coating solution of an organic **SOG** prepared while taking into consideration the results of the foregoing evaluation, and thus have completed the present invention.

In. . . at least one member selected from the group consisting of ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, propylene glycol **monomethyl ether**, ethylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether, di-n-butyl ether, di-isobutyl ether, di-n-amyl ether, methyl n-amyl ketone, methyl isoamyl. . .

Moreover, . . . at least one member selected from the group consisting of ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, propylene glycol **monomethyl ether**, ethylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether, di-n-butyl ether, di-isobutyl ether, di-n-amyl ether, methyl n-amyl ketone, methyl isoamyl. . .

The. . . of organic substituent or any solution in which such siloxanes are dissolved in an organic solvent and examples thereof include **SOG** solutions for forming **SOG** films and organic **SOG** solutions. In this respect, the organic substituent may be at least one member selected from the group consisting of saturated. . .

Such. . . In this regard, if the degree of polymerization (number

of

repeating units) exceeds 500, the viscosity of a coating solution (**SOG** solution) comprising siloxane and a solvent becomes

extremely high, while if it is less than 2, the siloxane is easily. .

When carrying out the nuclear magnetic resonance (NMR) spectroscopic method, siloxanes such as **SOG** solution as a sample is first dissolved in a deuterio solvent. The deuterio solvent herein used is not restricted to any specific one insofar as it does not cause any separation of components of the **SOG** solution from the same through the addition of the solvent and examples thereof usable herein include deuterio chloroform, deuterio acetone. . .

The . . . out that there is a close relation between the chemical structure of siloxanes and the characteristic properties of the resulting **SOG** film.

According . . . value y in the chemical formula is not less than 0.8 and not more than 1.3 unlike the conventional organic **SOG** (wherein y ranges from 0.3 to 0.6) and that the siloxane oligomer has a random structure while the conventional organic **SOG** includes a ladder siloxane having a regular structure.

The . . . value y is less than 0.8, the resulting film exhibits characteristic properties similar to those observed for the usual organic **SOG** and accordingly, the insulating films obtained are those simply having the shrinkage factor, water absorption, ability of flattening and dielectric. . .

In . . . is improved. Although there has not yet been developed any appropriate parameter for defining the random structure, the conventional organic **SOG** is liable to have a regular structure even if the value y is increased and accordingly, it is insufficient

in.

Examples . . . invention and accordingly can be used in the invention

are ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, propylene glycol **monomethyl ether**, ethylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether, di-n-butyl ether, di-isobutyl ether, di-n-amyl ether, methyl n-amyl ketone, methyl isoamyl. . .

If . . . oligomer is condensed and hardened. This phenomenon permits the leveling of a considerably wider area as compared with the conventional **SOG**.

The organic **SOG** coating solution having such characteristic properties can be prepared by the method for preparing a coating solution according to the. . .

This method is roughly identical to the conventional method for forming a film of an organic **SOG**, but the present invention is characterized in that the dried coating solution is maintained at a temperature of not less. . . .degree.C and not more than

300.degree.C

for not less than 30 seconds, in the light of the fact that the **SOG** of the present invention has a self-fluidization temperature of not less than 150.degree.C and not more than 300.degree.C , to thus complete the surface-leveling while making use of the self-fluidizing ability of the **SOG**. More specifically, a film obtained by applying the coating solution and then drying is again fluidized within the foregoing temperature. . . ensure flatness of the surface over a wide area. The subsequent steps are no more than the usual ones called **SOG** curing steps.

A siloxane oligomer contained in a commercially available organic **SOG** was inspected for the rates of the foregoing structural units (a), (b), (c) and (d) present therein and the contents of organic substituents present therein. In this Example, two kinds of organic **SOG**'s, i.e., Sample A (SF 1014 available from Sumitomo Chemical Co., Ltd.) and Sample B (Type 12000T available from Tokyo Ohka. . . Each organic **SOG** (Sample A or B; 1.5 ml each) and tris(acetylacetonato) Cr(III) (about 40 mg) were added to and dissolved in 1.5. . .

As . . . method permits easy determination of the rates of the

structural units (a), (b), (c) and (d) present in an organic
SOG and the contents of organic substituents present therein.

<image>

First of all, a coating solution of the present invention for forming
SOG films was prepared according to the following procedures
according to the method of the fourth embodiment of the present
invention.. . .

It is found that excellent flatness can be ensured through the use of
either of the **SOG**'s according to the present invention.

<image> <image>

Therefore, . . . to chemicals and the water resistance. Moreover,
the

present invention has such an effect that the accurate quality control
of **SOG**'s used for forming an insulating film can be ensured
during the production of the **SOG**'s.

L3 ANSWER 7 OF 13 EUROPATFULL COPYRIGHT 1999 WILA

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 827188 EUROPATFULL ED 19980316 EW 199810 FS OS
TIEN Cleaning liquid for producing semiconductor device and process for
producing semiconductor device using same.
TIDE Reinigungsfluessigkeit fuer die Herstellung von Halbleiter-Anordnungen
und Verfahren zur Herstellung von Halbleiter-Anordnungen unter
Verwendung derselben.
TIFR Liquide de nettoyage pour composants semi-conducteurs et procede de
fabrication de composants semi-conducteurs utilisant ledit liquide de
nettoyage.
IN Torii, Yoshimi, c/o Hitachi, Ltd., Semi & Inte. Cir. Div., 20-1
Josuihon-cho 5-chome, Kodaira-shi, Tokyo, JP;
Sasabe, Shunji, c/o Hitachi, Ltd., Semi & Inte. Cir. Div., 20-1
Josuihon-cho 5-chome, Kodaira-shi, Tokyo, JP;
Kojima, Masayuki, c/o Hitachi, Ltd., Semi & Inte. Cir. Div., 20-1
Josuihon-cho 5-chome, Kodaira-shi, Tokyo, JP;
Usuami, Kazuhisa, c/o Hitachi, Ltd., Semi & Inte. Cir. Div., 20-1
Josuihon-cho 5-chome, Kodaira-shi, Tokyo, JP;
Tokunaga, Takafumi, Device Development Center, of Hitachi, Ltd., 2326,
Imai, Ome-shi, Tokyo, JP;
Hara, Kazusato, Device Development Center, of Hitachi, Ltd., 2326,
Imai,
Ome-shi, Tokyo, JP;
Ohira, Yoshikazu, Device Development Center, of Hitachi, Ltd., 2326,
Imai, Ome-shi, Tokyo, JP;
Matsui, Tsuyoshi, Texas Instruments Japan Ltd., 2350, Kihara,
Miho-mura,
Inashiki-gun, Ibaraki-ken, JP;
Gotoh, Hideto, Texas Instruments Japan Ltd., 2350, Kihara, Miho-mura,
Inashiki-gun, Ibaraki-ken, JP;
Aoyama, Tetsuo, Mitsubishi Gas Chem. Co. Inc., Niigata Res. Lab., 182,
Aza-Shinwari, Tayuhama, Niigata-shi, Niigata-ken, JP;
Hasemi, Ryuji, Mitsubishi Gas Chem. Co. Inc., Niigata Res. Lab., 182,
Aza-Shinwari, Tayuhama, Niigata-shi, Niigata-ken, JP;
Ikeda, Hidetoshi, Mitsubishi Gas Chem. Co. Inc., Niigata Res. Lab.,
182,
Aza-Shinwari, Tayuhama, Niigata-shi, Niigata-ken, JP;
Ishihara, Fukusaburo, Mitsubishi Gas Chem. Comp. Ins., Corp. Res. Lab.,
22, Wadai, Tsukuba-shi, Ibaraki-ken, JP;
Sotoaka, Ryuji, Mitsubishi Gas Chem. Comp. Ins., Corp. Res. Lab., 22,
Wadai, Tsukuba-shi, Ibaraki-ken, JP
PA MITSUBISHI GAS CHEMICAL COMPANY, INC., No. 5-2, Marunouchi 2-chome,
Chiyoda-ku, Tokyo, JP
PAN 287632
AG Tuerk, Gille, Hrabal, Leifert, Brucknerstrasse 20, 40593 Duesseldorf,
DE
AGN 100971
OS ESP1998015 EP 0827188 A2 980304
SO Wila-EPZ-1998-H10-T2b
DT Patent
LA Anmeldung in Englisch; Veroeffentlichung in Englisch
DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT;
R LI; R LU; R MC; R NL; R PT; R SE
PIT EPA2 EUROPÄISCHE PATENTANMELDUNG
PI EP 827188 A2 19980304

OD 19980304
AI EP 1997-113056 19970730
PRAI JP 1996-211217 19960809

DETDEN. . . The present invention relates to a cleaning liquid having extremely low corrosiveness to materials such as a metallic film and **SOG (Spin On Glass)** film and to a process for producing a high quality and highly reliable semiconductor device, said cleaning liquid being suitably. . . However, . . . the insulating film wherein via holes are formed. Nevertheless, the aforesaid treatment method, when applied to an insulating film of **SOG** silicon oxide or a metallic film made of aluminium or an aluminum-containing alloy, brings about, for

example, connection failure for. . .

A . . . methyl acetate, ethyl acetate, butyl acetate, methyl lactate, and ethyl lactate, glycols such as ethylene glycohol monobutyl ether, diethylene glycol **monomethyl ether** and diethylene glycol monoethyl ether, and sulfur compounds such as dimethyl sulfoxide and sulfolane.

According . . . hole forming step, the vicinity of a via hole, which via hole is formed particularly in the insulating layer including **SOG** layer, is freed from pollution and thus is cleaned, thus enabling sufficient connection of metallic wiring and the formation of.

L3 ANSWER 8 OF 13 EUROPATFULL COPYRIGHT 1999 WILA

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 822545 EUROPATFULL ED 19980215 EW 199806 FS OS
TIEN Optical component and spirobiindan polymer therefor.
TIDE Optisches Bauelement und Spirobiindan-Polymer dazu.
TIFR Composant optique et polymere de spirobiindane pour cette utilisation.
IN Otsuji, Atsuo, 2882-4-21, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Takuma, Keisuke, 1172-3-402, Kamikuratamachi, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Suzuki, Rihoko, 8-11-A-25, Isogo, Isogo-ku, Yokohama-shi, Kanagawa, JP;
Urakami, Tatsuhiko, 3-42-7, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Motoshima, Toshihiro, 2882-2-49, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Yamashita, Watura, Mitsui Kagaku Apaas 522, Hirabarumachi, Omuta-shi, Fukuoka, JP;
Yoshimura, Tomomi, 1959-128, Shinyoshidacho, Kohoko-ku, Yokohama-shi, Kanagawa, JP;
Shibuya, Atsushi, 3-42-7-516, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Sakata, Yoshihiro, 4-5-45-214, Dai, Kamakura-shi, Kanagawa, JP;
Oikawa, Hideaki, 3-42-7-212, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Ohta, Masahiro, 2-6-41, Komachi, Kamakura-shi, Kanagawa, JP;
Ajioka, Masanobu, 1172-3-202, Kamikuratamachi, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Takagi, Masatoshi, 2882-3-28, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Karasawa, Akio, 3-42-7, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP
PA MITSUI TOATSU CHEMICALS, INCORPORATED, 2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, JP
PAN 204177
AG Stuart, Ian Alexander et al, MEWBURN ELLIS York House 23 Kingsway, London WC2B 6HP, GB

AGN 50492
 OS ESP1998008 EP 0822545 A2 980204
 SO Wila-EPZ-1998-H06-T2a
 DT Patent
 LA Anmeldung in Englisch; Veroeffentlichung in Englisch
 DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT;
 R LI; R LU; R MC; R NL; R PT; R SE
 PIT EPA2 EUROPÄISCHE PATENTANMELDUNG
 PI EP 822545 A2 19980204
 OD 19980204
 AI EP 1997-305763 19970731
 PRAI JP 1996-201825 19960731
 JP 1996-204614 19960802
 JP 1996-204615 19960802
 JP 1996-331831 19961212
 JP 1996-331832 19961212
 JP 1996-331833 19961212

DETDEN. . . agent are as follows. The monovalent hydroxy aliphatic or aromatic compounds include methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol **monomethyl**

ether, cyclohexanol, benzyl alcohol, allyl alcohol, phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, 4-phenylphenol, 4-cyclohexylphenol, 4-n-octylphenol, 4-isooctylphenol, 4-nonylphenol, 4-methoxyphenol, 4-n-hexyloxyphenol, . . .

In . . . necessary, there may be added inorganic fillers such as talc, alumina, barium sulfate and magnesium oxide; thixotropy agents such as **aerogel**; melamine resins such as hexamethoxy melamine and hexabutoxy melamine; leveling agents such as silicone, fluorinated polymers and acrylate copolymers; color. . .

Specific . . . regulating agent are as follows. Monovalent hydroxy aliphatic or aromatic compounds include methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol

monomethyl ether, cyclohexanol, benzyl alcohol, allyl alcohol, phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, 4-phenylphenol, 4-cyclohexylphenol, 4-n-octylphenol, 4-isooctylphenol, 4-nonylphenol, 4-methoxyphenol, 4-n-hexyloxyphenol, . . .

Examples . . . such a molecular-weight regulating agent include monovalent aliphatic hydroxy compounds such as methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol

monomethyl ether, cyclohexanol, benzyl alcohol and allyl alcohol;

aromatic hydroxy compounds such as phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, . . .

In . . . there may be added inorganic fillers such as talc, silica, alumina, barium sulfate and magnesium oxide; thixotropy agents such as **aerogel**; melamine resins such as hexamethoxy melamine and hexabutoxy melamine; leveling agents such as silicone, fluorinated polymers and acrylate copolymers; color. . .

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 844283 EUROPATFULL ED 19980610 EW 199822 FS OS
TIEN Curable resin composition and cured products.
TIDE Haertbare Harzzusammensetzung und gehaertete Produkte.
TIFR Compositions de resine durcissable et produits reticules.
IN Kurosawa, Takahiko, 3-3-1-201, Namiki, Tsukuba-shi, Ibaraki, JP;
Yamada, Kinji, 2-18-33-M1-2, Umezono, Tsukuba-shi, Ibaraki, JP;
Matsubara, Minoru, 1-23-5-102, Sengen, Tsukuba-shi, Ibaraki, JP;
Inoue, Yasutake, 2-13-28-311, Kawaguchi, Tsuchiura-shi, Ibaraki, JP;
Shinoda, Tomotaka, 2-13-28-201, Kawaguchi, Tsuchiura-shi, Ibaraki, JP;
Gotou, Kouhei, 5-2-16-401, Matsuhira, Tsukuba-shi, Ibaraki, JP
PA JAPAN SYNTHETIC RUBBER CO., LTD., 2-11-24, Tsukiji, Chuo-ku, Tokyo-to, JP
PAN 225751
AG Waechtershaeuser, Guenter, Prof. Dr., Patentanwalt, Tal 29, 80331 Muenchen, DE
AGN 12711
OS ESP1998036 EP 0844283 A1 980527
SO Wila-EPZ-1998-H22-T1a
DT Patent
LA Anmeldung in Englisch; Veroeffentlichung in Englisch
DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT; R LI; R LU; R MC; R NL; R PT; R SE
PIT EPAL EUROPÄISCHE PATENTANMELDUNG
PI EP 844283 A1 19980527
OD 19980527
AI EP 1997-120273 19971120
PRAI JP 1996-323361 19961120
JP 1996-327950 19961122
DET DEN Materials such as SiOF, organic **SOG** (**Spin on Glass**), fluorocarbon polymer, polyimide, polyparaxylylene, and benzocyclobutene polymer, for example, are currently known as materials for low dielectric constant insulating film. . . . However, . . . films such as films of silicon oxide which are used for semiconductor devices. The organic materials such as an organic **SOG**, polyimide resin, polyparaxylylene, and benzocyclobutene polymer, on the other hand, have poor heat resistance and moisture resistance. All these insulating. . . . Any . . . ether, i-propyl ether, n-butyl ether, n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, dioxolane, 4-methyl dioxolane, dioxane, dimethyldioxane, ethylene glycol **monomethyl ether**, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol mono-2-ethyl butyl. . . monophenyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol di-n-propyl ether, ethylene glycol di-n-butyl ether, diethylene glycol **monomethyl ether**, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, diethylene glycol dimethyl ether, . . . ethoxy triglycol, tetraethylene glycol dimethyl ether, tetraethylene glycol diethyl ether, tetraethylene glycol di-n-propyl ether, tetraethylene glycol di-n-butyl ether, propylene glycol **monomethyl ether**, dipropylene glycol **monomethyl ether**, tripropylene glycol **monomethyl ether**, tetrahydrofuran, 2-methyl tetrahydrofuran, ester-based solvents such as

diethylene carbonate, .gamma.-butyrolactone, .gamma.-valerolactone, methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl. . . . benzyl acetate, cyclohexyl acetate, 1-methylcyclohexyl acetate, 2-methylcyclohexyl acetate, 3-methylcyclohexyl acetate, 4-methylcyclohexyl acetate, n-nonyl acetate, methyl acetoacetate, ethyl acetoacetate, ethylene glycol **monomethyl ether** acetate, ethylene glycol monoethyl etheracetate, diethylene glycol **monomethyl ether** acetate, diethylene glycol monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, ethylene glycol mono-n-butyl ether acetate, diethylene glycol mono-n-propyl ether acetate, diethylene glycol mono-n-butyl ether acetate, propylene glycol **monomethyl ether** acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, glycol diacetate, methoxytriglycol acetate, ethyl propionate, n-propyl propionate, i-propyl. . . . Given i-propyl ether, n-butyl ether, n-hexyl ether, 2-ethylhexyl ether, ethylene oxide, 1,2-propylene oxide, dioxorane, 4-methyl dioxorane, dioxane, dimethyl dioxane, ethylene glycol **monomethyl ether**, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-n-hexyl ether, ethylene glycol mono-2-ethyl butyl. . . . ethylene glycol di methyl ether, ethylene glycol di ethyl ether, ethylene glycol di-n-propyl ether, ethylene glycol di-n-butyl ether, diethylene glycol **monomethyl ether**, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-n-hexyl ether, diethylene glycol dimethyl ether,. . . . ether, ethoxytriglycol, tetraethylene glycol dimethyl ether, tetraethylene glycol diethyl ether, tetraethylene glycol di-n-propyl ether, tetraethylene glycol di-n-butyl ether, propylene glycol **monomethyl ether**, dipropylene glycol **monomethyl ether**, tripropylene glycol **monomethyl ether**, tetrahydrofuran, and 2-methyl tetrahydrofuran; ester-based solvents such as diethylene carbonate, .gamma.-butyrolactone, .gamma.-valerolactone, methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate,. . . . benzyl acetate, cyclohexyl acetate, 1-methylcyclohexyl acetate, 2-methylcyclohexyl acetate, 3-methylcyclohexyl acetate, 4-methylcyclohexyl acetate, n-nonyl acetate, methyl acetoacetate, ethyl acetoacetate, ethylene glycol **monomethyl ether** acetate, ethylene glycol monoethyl ether acetate, diethylene glycol **monomethyl ether** acetate, diethylene glycol monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, ethylene glycol mono-n-butyl ether acetate, diethylene glycol mono-n-propyl ether acetate, diethylene glycol mono-n-butyl ether acetate, propylene glycol **monomethyl ether** acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, glycol diacetate, methoxy triglycol acetate, ethyl propionate, n-propyl propionate,. . . . Referring which a transistor has been formed a first insulating film 2 is formed from suitable material such as SiOF, organic SOG, fluorocarbon polymer, polyimide, polyparaxylylene, benzocyclobutene polymer, or the like. A first wiring layer 3 is then formed on this first. . . .

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 857740 EUROPATFULL ED 19980823 EW 199833 FS OS
 TIEN Stable particulate dispersions.
 TIDE Stabile teilchenfoermige Dispersionen.
 TIFR Dispersion stables de particules.
 IN Okoroafor, Michael O., 274 Jefferson Street, Export, PA 15632, US;
 McDonald, William H., 803 Dog Wood Trail, Cranberry Township, PA 16066,
 US;
 Wang, Alan E., 3870 Anjou Lane, Hoffman Estates, IL 60195, US
 PA BASF CORPORATION, 3000 Continental Drive North, Mount Olive, New Jersey
 07828-1234, US
 PAN 612862
 AG Abel, Manfred et al, BASF Aktiengesellschaft Patentabteilung ZDX - C6,
 67056 Ludwigshafen, DE
 AGN 75701
 OS ESP1998054 EP 0857740 A2 980812
 SO Wila-EPZ-1998-H33-T1a
 DT Patent
 LA Anmeldung in Englisch; Veroeffentlichung in Englisch
 DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT;
 R LI; R LU; R MC; R NL; R PT; R SE
 PIT EPA2 EUROPAEISCHE PATENTANMELDUNG
 PI EP 857740 A2 19980812
 OD 19980812
 AI EP 1998-101986 19980205
 PRAI US 1997-795736 19970205

DETDEN. . . formulations to facilitate foam formation. See, for example,
 U.S. Patent No. 4,751,251. It has been proposed that silica, e.g.,
 silica **aerogel**, be added to rigid polyurethane foam
 formulations to enhance the insulating properties of such foams when
 fluorocarbon blowing agents are. . .
 It . . . particulate dispersion" is meant a dispersion of a solid
 particulate material(s), e.g., a silica such as precipitated silica or
 silica **aerogel**, in a liquid medium (continuous phase) wherein
 the particulate material(s) does not agglomerate and/or settle within a
 period of three. . .
 Preferred . . . include, but are not limited to: propylene
 carbonate;
 2-methoxyethyl ether; dipropylene glycol, methyl ether; triethylene
 glycol, dimethyl ether; triethylene glycol, **monomethyl**
ether; tripropylene glycol, **monomethyl ether**
 ; methyl-2,5-dihydro-2,5-methoxy-2-furancarboxylate;
 1-methoxy-2-methylpropylene oxide; 2-methoxy ethyl acetoacetate;
 diethylene glycol, **monomethyl ether**,
 2-methoxy-1,3-dioxolane; methoxyacetone; methoxyacetaldehyde,
 dimethylacetal; methoxyacetaldehyde diethyl acetal; 2,5-dimethoxy
 tetrahydrofuran; 2,5-dimethoxy-3-tetrahydrofurano carboxaldehyde;
 2,2-dimethoxy propane; 1,2-dimethoxy propane and dimethoxy methane.
 Examples of. . .
 Classes . . . as calcium carbonate; metal oxides such as iron oxide;
 talc; mica; and silicas such as precipitated silicas, fumed silicas,
 silica **aerogels**, hydrophobic silicas, and hydrophilic silicas.
 The . . . rigid polyurethane foams, the preferred particulate
 material is silica. Classes of silica that may be used include, for
 example, silica **aerogels**, fumed silicas, precipitated silicas,
 and in particular hydrophobic and hydrophilic precipitated silicas.
 Preferred particulate materials may be selected from the group
 consisting of fumed silica, precipitated silica, silica **aerogel**

, and mixtures of such silicas.

L10 ANSWER 72 OF 259 EUROPATFULL COPYRIGHT 1999 WILA

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 854504 EUROPATFULL ED 19980802 EW 199830 FS OS
TIEN Coating solutions for use in forming bismuth-based ferro-electric thin films, and ferro-electric thin films, ferro-electric capacitors and ferro-electric memories formed with said coating solutions, as well as processes for production thereof.
TIDE Ueberzugsloesungen fuer die Verwendung in der Herstellung von ferroelektrischen Wismuth enthaltenden duennen Schichten, ferroelektrische duenne Schichten, ferroelektrische Kondensatoren und ferroelektrische Speicher, die mit diesen Ueberzugsloesungen hergestellt sind und ein Verfahren zu deren Herstellung.
TIFR Solutions de revetement pour utilisation dans la formation de films minces ferroelectriques contenant du bismuth, et films minces ferroelectriques, condensateurs ferroelectrique et memoires ferroelectriques formees avec ces solutions de revetements ainsi que des procedes pour leur production.
IN Sawada, Yoshihiro, 1-27-17, Kaminagaya, Konan-ku, Yokohama-shi, Kanagawa-ken, JP;
Hashimoto, Akira, 5-14-10, Bessho, Minami-ku, Yokohama-shi, Kanagawa-ken, JP;
Koiwa, Ichiro, c/o Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome, Minato-ku Tokyo, JP;
Mita, Juro, c/o Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome, Minato-ku Tokyo, JP;
Okada, Yukihisa, c/o Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome, Minato-ku Tokyo, JP;
Kanehara, Takao, c/o Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome, Minato-ku Tokyo, JP;
Kato, Hiroyo, c/o Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome, Minato-ku Tokyo, JP
PA TOKYO OHKA KOGYO CO., LTD., 150, Nakamaruko Nakahara-ku, Kawasaki-shi Kanagawa-ken, JP;
Oki Electric Industry Co., Ltd., 7-12, Toranomom 1-chome Minato-ku, Tokyo, JP
PAN 301511; 225692
AG Hansen, Bernd, Dr. Dipl.-Chem. et al, Hoffmann Eitle, Patent- und Rechtsanwaelte, Arabellastrasse 4, 81925 Muenchen, DE
AGN 4924
OS ESP1998049 EP 0854504 A1 980722
SO Wila-EPZ-1998-H30-T2b
DT Patent
LA Anmeldung in Englisch; Veroeffentlichung in Englisch
DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT; R LI; R LU; R MC; R NL; R PT; R SE
PIT EPAL EUROPÄISCHE PATENTANMELDUNG
PI EP 854504 A1 19980722
OD 19980722
AI EP 1998-100704 19980116
PRAI JP 1997-19834 19970118
JP 1997-185872 19970626
DETDEN The present invention relates to **coating** solutions for use in forming Bi-based ferroelectric thin films, and ferroelectric thin films,

ferroelectric capacitors and ferroelectric memories formed with said **coating** solutions, as well as processes for production thereof.

More particularly, the invention relates to **coating** solutions that lead to only a small amount of separation (segregation, precipitation) of excessive metallic elements' particles, little leakage

current, . . . have good keeping quality. The invention also relates to ferroelectric thin films, ferroelectric capacitors and ferroelectric memories formed with such **coating** solutions, as well as processes for the production thereof.

Thin . . . of repeated polarization switching. This has spotlighted the potential use of BLSF thin films as materials for the fabrication of

semiconductor memories and sensors (T. Takenaka, "Bismuth Layer-Structured Ferroelectrics and Their Grain Orientation" in Report of the Workshop on Applied Electronics. . . .

Such BLSF thin films can be formed by various methods including sputtering, CVD and **coated** film formation. However, due to the many metal oxides that have to be incorporated as constituents, sputtering and CVD techniques. . . . films at desired levels; hence, these techniques are not suitable for practical applications, particularly on large-diameter substrates. In contrast, the **coated** film formation technique does not need expensive apparatus and can **deposit** films at relatively low cost; in addition, they provide ease in controlling the composition of ferroelectric thin films at desired levels. Therefore, the **coated** film process for the formation of BLSF thin films holds much promise for commercial use.

While several formulations have been proposed for use as **coating** solutions in the formation of BLSF thin films by the **coated** film process, two typical cases are those prepared by dissolving carboxylate (e.g., 2-ethylhexanate) of Sr and Bi and alkoxides. . . . pp. 5096-5099, 1995) and those prepared by dissolving 2-ethylhexanate of

Sr, Bi, Ta, Nb, Ti, etc. in xylene to form **coating** solutions of a metallo-organic decomposition (MOD) type (Proceedings of the 12th Ferroelectric Materials and their Applications meeting on May 24-27, 1995, Paper presented by Olympus Optical Co., Ltd. and Symetrix Corporation, 26-TC-10, pp. 139-140). However, these **coating** solutions have had various problems. First, the 2-ethylhexanate of the respective metal components has a long-chain (C.sub8.) organic group,

so a large portion of the **coating** solution is occupied by the organic content and there is much loss in the **coating** weight due to the burning out of the organic content in the process of film formation consisting of the application of the **coating** solution, baking of the applied **coating** and crystallization and a porous film will result. In addition, the surface morphology of the **coating** film is not satisfactory enough to provide for easy application to the fabrication of VLSI devices. Further in addition, in order to form a thin film using the applied **coating**, the applied **coating** has to be annealed twice at an elevated temperature of 800.ordm.C to ensure appropriate electrical characteristics thereof, however, this is problematic from the viewpoint of **semiconductor** fabrication process. It is pointed out that in the conventional BLSF-based **coating** solutions, high-volatility metals such as Bi are burnt out on forming a thin film, particularly during prebaking and annealing, and. . . . advance high-volatility Bi excessively in a molar amount 1.15 - 1.3 times as great as the stoichiometric amount to the **coating** solution in order to compensate the loss of burnout of Bi. Even when using a **coating** solution having a composition out of the theoretical amount (stoichiometric amount) as mentioned above, it was difficult to form a. . . . cause an increase in leakage current. When applying a ferroelectric memory processed by using the film above

to an actual **semiconductor** device memory having a very small area, problems such as film fatigue resulting from repeated polarization switching, increase in leakage. . . . Although . . . It was therefore difficult to form a film having a composition close to the stoichiometric composition in the conventional BLSF-based **coating** solutions.

The prior art **coating** solutions have further problems. The long-chained metal carboxylates (metallic soaps) of monobasic acids which are commonly used in the **coating** solutions are generally slightly soluble in polar solvents and, hence, aromatic solvents such

as xylene and toluene are used to prepare the **coating** solutions. However, the **coating** solutions using such aromatic solvents have to be stored in glass or metallic containers in order to ensure that the . . . atmosphere. On the other hand, glass and metallic containers have the disadvantage that metallic components will

dissolve out into the **coating** solution and this is by no means desirable in the art of **semiconductor** fabrication which hates the contamination with metallic impurities. Under these circumstances, it is preferred to use polyethylene or polypropylene containers. . . .

If . . . air, they have only poor keeping quality and practically acceptable levels of reproduction cannot be achieved in the result of **coating** operations.

Under these circumstances, it has been Strongly desired to develop a **coating** solution that is capable of forming highly dense films of good quality, which lead to little leakage current and are excellent in hydrogen heat treatment resistance and pressure resistance, with minimal **coating** weight loss due to the burning of the organic content and separation (segregation) of metallic elements in the **coating** solution and which is soluble in practical organic solvents and which have good keeping quality.

An object of the present invention is therefore to provide a **coating** solution that contains an organometallic compound soluble in practical organic solvents, that leads to little leakage current, is excellent in. . . capable of forming dense Bi-based ferroelectric thin films, that has good keeping quality and that

ensures highly reproducible results in **coating** operations. Another object of the invention is to provide Bi-based ferroelectric thin films using the **coating** solution. Yet another object of the invention is to provide a ferroelectric capacitor and a ferroelectric memory using the **coating** solution, particularly to provide Bi-based ferroelectric thin films, a ferroelectric capacitor and a ferroelectric memory permitting

inhibition of separation (segregation). . . .

As . . . made in order to solve the foregoing problems, the present inventors obtained the following findings. Any of the conventional BLSF-based **coating** solutions is prepared by only mixing metal carboxylates, metal alkoxide compounds and the like in an organic solvent. This forms. . . as a ferroelectric capacitor or a ferroelectric memory through further improvement of hydrolysis rate and hence inorganic properties of the **coating** solution by increasing keeping stability and polarity of the **coating** solution during or after hydrolysis resulting from reaction of the stabilizer. The inventors have accomplished the present invention as a.

. . . More specifically, the present invention relates to a **coating** solution for use in forming Bi-based ferroelectric thin film containing Bi, metallic element A (which is at least one metallic. . . . The invention relates to a ferroelectric thin film formed by applying the foregoing **coating** solution onto an electrode on a

substrate, optionally exposing the applied **coating** to a humidified atmosphere and then baking (annealing) the **coating**.

In . . . a ferroelectric thin film by the steps of:

(I) forming an electrode over a substrate;

(II) applying a **coating** solution for use in forming a ferroelectric thin film onto the electrode; and

(III) annealing the applied **coating**;

wherein the process uses, as the **coating** solution for use in forming ferroelectric thin films, a Bi-based **coating** solution for use in forming ferroelectric thin films, containing Bi, metallic element A (which is at least one metallic element. . . . Further, . . . producing a ferroelectric capacitor by the steps of:

(I) forming an electrode over a substrate;

(II) applying a **coating** solution for use in forming a ferroelectric thin film onto the electrode;

(III) annealing the applied **coating** to form a ferroelectric thin film; and

(IV) forming an electrode over the ferroelectric thin film; wherein the process uses, as the **coating** solution for use in forming ferroelectric thin films, a Bi-based **coating** solution for use in forming ferroelectric thin films, containing Bi, metallic element A (which is at least one metallic element. . . .

The **coating** solution for use in forming Bi-based ferroelectric thin films of the invention contains Bi, metallic element A (which is at. . . .

It is preferable to use, as the aforesaid **coating** solution for use in forming a Bi-based ferroelectric thin film, a **coating** solution for use in forming Bi-based ferroelectric thin films, wherein the Bi-based ferroelectric thin films are represented by the general.

The **coating** solution of the invention contains organometallic compounds obtainable by hydrolyzing the foregoing composite metal alkoxides with water alone or in. . . .

In order to perform the hydroxylic reaction, water alone or in combination with a catalyst may be added to the **coating** solution, which then is stirred at 20-50.ordm.C for several hours to several days. Any catalysts such as metal alkoxides that. . . . inorganic alkali catalysts such as sodium hydroxide and potassium hydroxide, metallic ions of sodium and potassium may remain in the **coating** solution and therefore may exert an adverse effect on the electric properties of the film, and for nitrogen-containing alkali catalysts. . . .

Hydrolysis may also be performed by exposing the surface of the as-applied **coating** on an electrode to a humidified atmosphere at a temperature of about 50-120.ordm.C for about 10-60 minutes at a humidity. . . .

The . . . way limited to those set forth above and they may be selected as appropriate for the specific use of the **coating**.

The hydrolytic treatment is effective in not only reducing the organic content of the dried **coating** but also forming metaloxane bonds of metallic elements, and hence, the separation (segregation) of Bi and other metallic elements, as. . . . inorganic property. The eliminated organic groups are to be low-boiling-point alcohols and glycols. Those alcohols and glycols remain in the **coating** solution or the film, however, are evaporated together with the solvent in the drying step. Therefore, inorganic property of the. . . .

The above-mentioned stabilizer is for improving the keeping stability

of

the **coating** solution, and in the invention, at least one selected from the group consisting of carboxylic anhydrides, dicarboxylic acid monoesters, .beta.-diketones,. . . . Such . . . at least one alcohol as selected from among methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, amyl alcohol,

hexyl alcohol, **ethylene glycol monomethyl ether**, propylene glycol **monomethyl ether**, etc., by known methods.

Specific . . . formers such as hexafluoroacetylacetone that form metal halides after annealing are not suitable for use in the production of the **coating** solution of the invention since they form highly sublimable or volatile metal complexes.

The BLSF-based **coating** solution of the invention contains in advance Bi in a molar amount in excess of the stoichiometric amount, i.e., in . . .

Because . . . burnout loss of metallic elements in the film. It is thus possible to reduce the amount of Bi in the **coating** solution to in a molar amount 1 - 1.1 times as great as the stoichiometric amount. This makes it possible. . .

Composite . . . it possible to form a BLSF thin film whose percentage composition is closest to that of metallic elements in the **coating** solution.

The **coating** solution of the invention is produced by dissolving one of those reaction products (organometallic compounds) in organic solvents having oxygen. . .

Exemplary polyhydric alcohol-based solvents include **ethylene glycol monomethyl ether**, **ethylene glycol monoacetate**, diethylene glycol **monomethyl ether**, diethylene glycol monoacetate, propylene glycol monoethyl ether, propylene glycol monoacetate, dipropylene glycol monoethyl ether and methoxybutanol.

The selection of the most preferred solvent depends on specific **coating** conditions such as those of open spin **coating**, closed spin **coating**, liquid source misted chemical vapor deposition (LSM-CVD) and dip **coating**.

A method of producing a ferroelectric thin film and a ferroelectric memory using the **coating** solution of the invention will be described below with reference to Figs. 1 and 2.

As . . . conductive metal oxide thereof by a known technique such as sputtering or vapor deposition. The lower electrode 4 is then coated with the **coating** solution of the invention by a known technique such as spin **coating** or dip **coating** and the applied **coating** is dried at a temperature of 50-200.degree.C, followed by prebaking at a temperature of 200-700.degree.C. Preferably, the process from the application of the **coating** solution to the prebaking of the dried **coating** is repeated several times until a desired film thickness is attained.

As . . . is possible to reduce the amount of separation (segregation) and the burnout loss of metallic elements such as Bi in **coating** and annealing processes by converting metal alkoxides to composite metal alkoxides, followed by hydrolyzing them. Possibility of reducing the amount. . .

By . . . practical polar solvents. As a result, a polycondensation reaction could be allowed to proceed through the sol-gel method in the **coating** solution by a sufficient degree, and production of inorganic bonds (metalloxane bonds) such as Bi-O-Bi, Bi-O-Ta, Bi-O-Sr, and Ta-O-Bi-O-Sr could. . . further reduce separation (segregation) and burnout loss of Bi and other metallic elements, and enhance the inorganicity of the entire **coating** solution.

Even if the **coating** solution is not rendered fully inorganic by the sol-gel method (hydrolytic treatment) or even in the case of the **coating** solution which is not subjected to hydrolytic treatments at all, the as-applied **coating** on the substrate may be exposed to a humidified atmosphere for a certain period preceding the annealing step in forming a **coating** film as described above and by so doing, hydrolytic polycondensation will proceed to render the

coating sufficiently inorganic to form a dense film.

An excessive hydrolytic treatment in the **coating** solution may potentially increase the viscosity of the **coating** solution gel or change its properties with time. The above-mentioned hydrolytic treatment of the as-applied **coating** prior to annealing in a forming a **coating** film is effective in order to avoid these possibilities.

It should be noted here that if an MOD **coating** solution made of a metal carboxylate having a long-chain organic group as described

in

connection with the prior art is applied onto a substrate and if the as-applied **coating** is subjected to a hydrolytic treatment prior to annealing in forming a **coating** film, the progress of the reaction is either uneven or negligible and there is a limit on

the

denseness of the **coating** to be finally formed.

It should also be noted that the contents of Bi, and metallic elements

A

and B in the **coating** solution for use in forming a Bi-based ferroelectric thin film are variable with the site and conditions of

the

application of the **coating** solution. Hence, appropriate formulations can be selected depending upon various conditions such as the type of the device to which. . . .

The . . . degree of composite alkoxylation can be selected in many ways depending upon various factors such as the use of the **coating** solution of the invention and the conditions under which it is to be employed (e.g., temperature, time, atmosphere and the. . .

Synthesis Example 1 (synthesis of **coating** solution 1)

(Preparation of a **coating** solution through hydrolysis with H.sub2O in a molar amount two times as great as mole of a composite metal alkoxide. . . .

Then, . . . contained in the solution was dropped and the resultant solution was stirred at 25.degree.C for two hours to synthesize a **coating** solution 1 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 2 (synthesis of **coating** solution 2)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

Then, . . . in the solution was dropped, and the resultant mixed solution was stirred at 25.degree.C for two hours, thereby synthesizing a **coating** solution 2 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 3 (synthesis of **coating** solution 3)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into carboxylic anhydride form, followed by hydrolysis with. . . .

A **coating** solution 3 for forming a Bi-based ferroelectric thin film having a concentration of 10 wt% was synthesized in the same. . .

Synthesis Example 4 (synthesis of **coating** solution 4)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

A **coating** solution 4 for forming a Bi-based ferroelectric thin film having a concentration of 10 wt% was synthesized in the same. . .

Synthesis Example 5 (synthesis of **coating** solution 5)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi and a Ta alkoxide into .beta.-diketonized and glycolized one,

Then, . . . contained in that solution was dropped, and the resultant

solution was stirred at 25.degree.C for two hours, thereby synthesizing a **coating** solution 5 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 6 (synthesis of **coating** solution 6)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Bi, Ta and an Sr alkoxide into .beta.-diketonize and glycolize, followed. . . .

Then, . . . alkoxide contained in that solution was dropped, and the solution was stirred at 25.degree.C for two hours, thereby synthesizing a **coating** solution 6 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 7 (synthesis of **coating** solution 7)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Ta and a Bi alkoxide into .beta.-diketonized and glycolized one, followed. . . .

Then, . . . alkoxide contained in that solution was dropped, and the solution was stirred at 25.degree.C for two hours, thereby synthesizing a **coating** solution 7 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 8 (synthesis of **coating** solution 8)

(Preparation of a **coating** solution through hydriding a composite metal alkoxide of Sr, Bi, Ta with H.sub2.O in a molar amount two times as. . . .

Then, . . . that solution was dropped, and the resultant solution

was

refluxed while heating to 80.degree.C for two hours, thereby synthesizing a **coating** solution 8 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt%.

Synthesis Example 9 (synthesis of **coating** solution 9)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

A **coating** solution 9 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt% was synthesized in the same. . . .

Synthesis Example 10 (synthesis of **coating** solution 10)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

A **coating** solution 10 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt% was synthesized in the

same.

Synthesis Example 11 (synthesis of **coating** solution 11)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

A **coating** solution 11 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt% was synthesized in the

same.

Comparative Synthesis Example 1 (synthesis of comparative **coating** solution 1)

(Preparation of a **coating** solution through conversion of a composite metal alkoxide of Sr, Bi, Ta into .beta.-diketonized and glycolized one, followed by hydrolysis. . . .

A comparative **coating** solution 1 for forming a Bi-based ferroelectric thin film, having a concentration of 10 wt% was synthesized in the same. . . .

Comparative Synthesis Example 2 (synthesis of comparative **coating** solution 2)

(Preparation of a **coating** solution through mixture of metal alkoxides of Sr, Bi and Ta)

After . . . distilled off under reduced pressure, and the solution was concentrated to a concentration of 10 wt%, thereby synthesizing a

comparative **coating** solution 2 for forming a Bi-based ferroelectric thin film.

Then, **coating** solutions 1 to 10 obtained in the foregoing Synthesis Examples and comparative **coating** solutions 1 and 2 obtained in Comparative Synthesis Examples were **coated** onto the aforesaid Pt lower electrode by means of a spin **coater** at 500 rpm for five seconds and then at 2,000 rpm for 30 seconds. After drying at 150.degree.C for 30 minutes, prebaking was conducted at 650.degree.C for 30 minutes. The foregoing operations from **coating** to prebaking were repeated ten times. After that, a temperature was elevated in an oxygen atmosphere from 25.degree.C to 800.degree.C. . . . In Example 11, a 300 nm-thick ferroelectric thin film was formed in the same manner as above except that, using the **coating** solution 11, the prebaking temperature was changed from 650.degree.C to 450.degree.C and the primary annealing temperature, from 800.degree.C

to

700.degree.C. . . . The ferroelectric capacitors formed with the **coating** solutions 1 to 11 exhibited satisfactory hysteresis curves with a high square ratio at an applied voltage within a range. . . . 700.degree.C. The results are shown in Figs. 4 to 14. Figs. 4 to 13 respectively correspond to Examples using the **coating** solutions 1 to 10 (Examples 1 to 10). Fig. 14 illustrates hysteresis curves at an applied voltage of 10 V. . . .

When using the comparative **coating** solution 1 or 2, a satisfactory hysteresis curve with a high square ratio is unavailable. When using the comparative **coating** solution 1, hysteresis property can no more be obtained at an applied voltage of over 6.5 V. When using the comparative **coating** solution 2, a hysteresis property becomes unavailable at an applied voltage of over 5.5 V, suggesting that both the comparative **coating** solutions had a low voltage resistance. These results are shown in Figs. 15

(Comparative

Example 1) and 16 (Comparative Example. . . . A ferroelectric capacitor formed with the **coating** solution 4 was subjected to a heat treatment in an atmosphere comprising 10% hydrogen and 90% nitrogen at 400.degree.C for. . . . It is confirmed from the above that the ferroelectric capacitor formed by the use of the **coating** solution 4 containing Bi in a molar amount 1.05 times as great as the stoichiometric amount and subjected

to

a. . . . The **coating** solution 2 and the comparative **coating** solution 2 were evaluated for the above Examples and Comparative Examples in the same manner as above except that the. . . . The ferroelectric capacitor formed with the use of the **coating** solution 2 showed a satisfactory hysteresis curve with a high square ratio at an applied voltage of 2 to 18. . . . When using the comparative **coating** solution 2, on the other hand, a satisfactory hysteresis curve with a high square ratio is unavailable, and at an. . . . According to the present invention, as described above in detail, there is provided a **coating** solution for forming a Bi-based ferroelectric thin film, which is capable of forming a dense film

hardly

suffering separation of. . . . leakage current, and excellent in hydrogen heat treatment resistance and voltage resistance, with a high keeping stability. By using this **coating** solution, it is possible to form a ferroelectric thin film, a ferroelectric capacitor and a ferroelectric memory at a low. . . .

AN 767467 EUROPATFULL ED 19970429 EW 199715 FS OS
 TIEN Low dielectric resin composition.
 TIDE Harzmasse mit niedriger Dielektrizitaetskonstante.
 TIFR Composition de resine ayant une constante dielectrique faible.
 IN Yokotsuka, Shunsuke, c/o Asahi Glass Co., Ltd., Chuo Kenkyusho, 1150
 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa, JP;
 Serita, Aya, c/o Asahi Glass Co., Ltd., Chuo Kenkyusho, 1150
 Hazawa-cho,
 Kanagawa-ku, Yokohama-shi, Kanagawa, JP;
 Aosaki, Ko, c/o Asahi Glass Co., Ltd., Chuo Kenkyusho, 1150 Hazawa-cho,
 Kanagawa-ku, Yokohama-shi, Kanagawa, JP;
 Matsukura, Ikuo, c/o Asahi Glass Co., Ltd., Chuo Kenkyusho, 1150
 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa, JP;
 Narita, Takenori, No. 2-9, Yamazaki-Ryo 4-chome, Higashi-cho,
 Hitachi-shi, Ibaraki-ken, 317, JP;
 Morishima, Hiroyuki, No. 19-3, 2-chome Kamiai-cho, Hitachi-shi,
 Ibaraki-ken, 317, JP;
 Uchimura, Shunichiro, No. 22-10, 4-chome Tajiri-cho, Hitachi-shi,
 Ibaraki-ken, 317, JP
 PA ASahi GLASS COMPANY LTD., 1-2, Marunouchi 2-chome, Chiyoda-ku Tokyo
 100,
 JP;
 HITACHI CHEMICAL CO., LTD., 1-1, Nishishinjuku 2-chome, Shinjuku-ku,
 Tokyo 163-04, JP
 PAN 242771; 1192837
 AG Mueller-Bore & Partner Patentanwaelte, Grafinger Strasse 2, 81671
 Muenchen, DE
 AGN 100651
 OS ESP1997020 EP 0767467 A2 970409
 SO Wila-EPZ-1997-H15-T2b
 DT Patent
 LA Anmeldung in Englisch; Veroeffentlichung in Englisch
 DS R DE; R FR; R GB; R IT
 PIT EPA2 EUROPÄISCHE PATENTANMELDUNG
 PI EP 767467 A2 19970409
 OD 19970409
 AI EP 1996-115073 19960919
 PRAI JP 1995-243228 19950921
 DETDEN In recent years, as miniaturization, high integration and high
 densification progress for **semiconductor** devices or
 multi-layered circuit boards, insulating materials having low
 dielectric
 constants have been desired which contribute to shortening the time of
 signal propagation delay. Presently widely used as a buffer coat
 film of a **semiconductor** device, a passivation film of a
semiconductor device, an interlayer dielectric film of a
semiconductor device, an .alpha.-ray shielding film of a
semiconductor device or an interlayer dielectric film of a
 multi-layered circuit board, are a silicon oxide film, a silicon
 nitride
 film, . . .
 In . . . aliphatic fluorine resin is insoluble in a solvent, whereby
 it has been difficult to form a thin film uniformly by **coating**
 . Whereas, as disclosed in Japanese Unexamined Patent Publications No.
 238111/1988 and No. 260932/1988 and U.S. Patent 4,754,009, fluorine
 resins (dielectric. . .
 A . . . and a metal does not diffuse into it. European Patent
 0393682
 discloses its application to a protective film for a
semiconductor device, and Japanese Unexamined Patent Publication
 No. 283827/1993 discloses its application to an insulating film for a
 multi-layered circuit board. . .
 However, . . . modulus of elasticity is small, and the linear
 expansion coefficient is as large as from 50 to 100 ppm. A

semiconductor device or a multi-layered circuit board is a composite with a wiring metal (linear expansion coefficient: about 20 ppm/degree.C) or. . .

As disclosed, for example, in a collection of papers reported at Symposium for **Semiconductors** and **Integrated**

Circuit Technology, pp66, vol.48 (1995), a resin having a glass transition temperature of about 350.degree.C has been developed by improving the. . .

Further, . . . adhesion of particles to one another is likely to occur, whereby it has been practically difficult to form a uniform **coating** film having a thickness of from 0.1 .mu.m to a few .mu.m.

Further, . . . if such surface treatment is carried out, the affinity

of the fluorine resin and the inorganic component in the formed **coating** film is not necessarily adequate. Accordingly, there has been a problem such that the mechanical strength is small, and the. . .

Accordingly, it is an object of the present invention to provide a low dielectric resin composition useful as e.g. a **coating** composition capable of forming a uniform **coating** film by overcoming a drawback such that it is mechanically soft particularly at a high temperature i.e. the modulus of. . .

The . . . invention provides a low dielectric resin composition comprising the following components (a) and (b), and the dielectric constant of a **coating** film formed by this composition being at most 3:

(a) a resin having functional groups in its molecule and. . .

A **coating** film formed by the resin composition of the present invention is a film having a dielectric constant of at most. . .

With respect to **semiconductor** devices, miniaturization, high integration and high densification are in progress, and along with the progress, noises and delay in signal propagation attributable to insulation films such as interlayer dielectric films, passivation

films,

buffer **coat** films or .alpha.-ray shielding films, have become problems to be solved. To solve such problems, it is effective to

apply.

Also . . . insulating film, along with the progress in miniaturization, high densification and high frequency of signals. Like in the case of **semiconductor** devices, it is effective to apply an insulating film having a low dielectric constant.

As . . . high temperature, or the linear expansion coefficient is large, which becomes a drawback when the resin is applied to a **semiconductor** device or a multi-layered circuit board.

A **semiconductor** device or a multi-layered circuit board is a composite with a wiring metal (linear expansion coefficient: about 20 ppm/degree.C) and. . . the linear expansion coefficient of the wiring metal or other inorganic insulating films, cracks are likely to form in the **coating** film, whereby the production yield is likely to decrease, or the reliability in the useful life of the **semiconductor** device or the multi-layered circuit board tends to decrease.

The present invention is intended to provide a low dielectric resin composition which is capable of forming a **coating** film which satisfies a dielectric constant of at most 3 which is indispensable to accomplish miniaturization, high densification and high integration,

and

a requirement of not impairing the production yield or the reliability in the useful life of the **semiconductor** device or the multi-layered circuit board, simultaneously. In the **coating** film formed by the resin composition of the present invention, the

resin

having a low dielectric constant and the cured. . .

It . . . the after-mentioned coupling agent (c) in a solution, so that a uniform solution can be obtained, and consequently, a uniform **coating** film can be obtained. From the viewpoint of compatibility with the partially hydrolyzed condensate (b), the functional groups in the . . .

The . . . from those having the above-mentioned functional groups

and

low dielectric constants. In order to make the dielectric constant of the **coating** film formed by the **coating** composition of the present invention to a level of at most 3, the dielectric constant of the resin (a) is required to be at most 3, preferably at most 2.8. Further, the modulus of elasticity of the **coating** film formed by the **coating** composition of the present invention, at a temperature of at least 200.degree.C, is at least the modulus of elasticity of. . .

The **coating** composition of the present invention comprises the above-mentioned resin (a) having functional groups in its molecule and

a

partially hydrolyzed. . .

The oxygen-containing hydrocarbon solvent may, for example, be an alcohol such as methanol, ethanol, propanol or butanol, an ether such

as

ethylene glycol monoethyl ether or **ethylene glycol monomethyl ether**, or a sulfoxide such as dimethylsulfoxide.

It . . . with the resin (a) with the partially hydrolyzed condensate (b) will thereby be improved, and the phase separation of a **coating** film will be suppressed, whereby the mechanical strength at a high temperature will further be improved. The crosslinking reaction between. . . partially hydrolyzed condensate (b) may take place in the state of the solution or during the step of forming the **coating** film. However, it is preferred that the crosslinking reaction partially takes place in the state of the solution, since the.

The . . . titanate coupling agent, or an aluminum coupling agent.

This silane coupling agent is different from the component (b) in the **coating** composition of the present invention, in that it is not a partially hydrolyzed condensate.

When . . . (2), if the amount is too much, the viscosity stability

of

the liquid deteriorates, and the electric properties of the **coating** film tend to be impaired, and the mechanical properties of the **coating** film at a high temperature will not be improved if the amount exceeds a certain level. Accordingly, the amount of. . .

The . . . may suitably be selected from the viewpoint of the desired viscosity of the solution or the film thickness of the **coating** film, within the range where the solid content dissolves. For example, in a case where a **coating** film having a film thickness of from 0.1 to 5 .mu.m is to be formed by a spin **coating** method, the solid content concentration may usually be set within a range of from 1 to 15 wt%.

To . . . of the partially hydrolyzed condensate (b), whereby the adhesion to the substrate will be improved, or the strength of the **coating** film will be improved.

As a method for forming a **coating** film on an article by the resin composition of the present invention, it is preferred to employ a method wherein the resin composition of the present invention

containing

a solvent is **coated** on the article, followed by heating and drying to evaporate the solvent. Here, to secure adequate adhesion to the substrate,. . .

The method for **coating** the composition of the present invention may, for example, be a spin **coating** method, a dipping method, a potting method, a die **coating** method or a

spray **coating** method, and the **coating** method may suitably be selected depending upon the shape of the article to be **coated**, the required film thickness, etc. When the composition of the present invention is to be applied to a buffer **coat** film for a **semiconductor** device, a passivation film for a **semiconductor** device, an interlayer dielectric film for a **semiconductor** device or an .alpha.-ray shielding film for a **semiconductor** device, a spin **coating** method is preferred, since the in-plane distribution of the film thickness will thereby be uniform. When it is applied to an interlayer dielectric

film

for a multi-layered circuit board, a die **coating** method as well as a spin **coating** method, is preferred as a method whereby high liquid yield is obtainable.

To form a **coating** film, a baking step is required after **coating**, to evaporate the solvent and to cure the partially hydrolyzed condensate of alkoxysilanes. The baking condition may suitably be selected depending upon e.g. the **coating** film thickness. For a sufficient curing reaction, a final baking at a temperature of from 200 to 450.degree.C is usually. . .

450.degree.C, is required. Unreacted alkoxysilyl groups or silanol groups will be a factor for increasing the dielectric constant of the **coating** film by themselves, and they may further be a water absorbing site, which causes an increase of the dielectric constant by water. Accordingly, it is advisable not to let them remain in the **coating** film as far as possible.

For the purpose of securing the surface smoothness of the **coating** film or improving a fine space filling property of the **coating** film, it is possible to add a prebaking step at a temperature of from 50 to 250.degree.C or to carry. . .

Further, depending upon the particular purpose, the **coating** film formed from the composition of the present invention and other films may be combined to form a composite film. For example, in an application to a passivation film for a **semiconductor** device or an interlayer dielectric film for a **semiconductor** device, an inorganic film may sometimes be formed as an under layer and/or an upper layer of the film formed. . .

By . . . of the metal wiring or to prevent downward diffusion of moisture which is likely to occur during curing when a **coating** film is formed from the composition of the present invention, whereby

it

is possible to prevent deterioration of the device. . .

Specifically, . . . CVD or plasma CVD. Further, formation of an inorganic film as an upper layer, may be carried out after the **coating** film formed from the composition of the present invention is polished by a so-called etch back method or a CMP. . . When . . . the inorganic film or the method of its formation, there will be a problem such that the adhesion to a **coating** film formed from the composition of the present invention is poor, or the **coating** film receives a damage such as film reduction during the formation of the inorganic film. To overcome such a problem, . . . using the thin film thereby formed, as a barrier layer, a silicon oxide film is formed thereon.

(2) The **coating** film formed from the composition of the present invention is firstly treated with energy rays to activate the surface, and. . .

Among these treatments, preferred as a treating method suitable for a mass production of **semiconductor** devices may, for example, be ultraviolet irradiation, laser beam irradiation, corona discharge treatment or plasma treatment. Particularly preferred is plasma treatment, whereby the damage to **semiconductor** devices will be minimum.

An . . . and a nitrogen gas, may preferably be mentioned as gasses which are capable of effectively activating the surface of a

coating film formed by the composition of the present invention and which is substantially free from bringing about film reduction.

In its application to a buffer **coat** film for a **semiconductor** device, a passivation film for a **semiconductor** device, an interlayer dielectric film for a **semiconductor** device, an .alpha.-ray shielding film for a **semiconductor** device or an interlayer dielectric film for a multi-layered circuit board, the **coating** film formed from the composition of the present invention may sometimes require fine processing. In such a case, the above-mentioned energy ray treatment, particularly the plasma treatment, is effective for preventing cissing at the time of **coating** a photoresist for photolithography. The fine processing method may be a known or well-known method such as a

wet

etching. . .

In the present invention, the **semiconductor** device may, for example, be a discrete **semiconductor** device, such as a diode, a transistor, a compound **semiconductor**, a thermistor, varistor or a thyristor; an **integrated circuit** (IC) device, such as a memory IC e.g. DRAM (dynamic random access memory), SRAM (static random access memory), EPROM (erasable. . .). The **coating** film formed by the composition of the present invention is applied as a buffer **coat** film, a passivation film, an interlayer dielectric film or an .alpha.-ray shielding film

for

a **semiconductor** device, whereby it is possible to attain high performance in e.g. reducing the time of signal propagation delay of a.

In the present invention, the multi-layered circuit board includes a high density circuit board such as MCM. By applying the **coating** film formed from the composition of the present invention as an interlayer dielectric film, it is possible to attain the. . . Then, with respect to each composition, the following evaluation (A) was carried out. On the other hand, a **coating** film was formed from the solution of the composition by a casting method, and the following evaluations (B) to (D). . . 350.degree.C.

(A) Appearance of the solution: The appearance of the solution was visually examined.

(B) Appearance of the **coating** film: The appearance of the **coating** film was visually examined.

linear

(C) Measurement for modulus of elasticity and measurement for expansion coefficient: By a TMA. . .

The solution of the composition obtained in Example 13 was **coated** by a spin **coater** and baked at 100.degree.C for 1 hour, then at 250.degree.C for 1 hour and then at 400.degree.C for 1 hour, to form a **coating** film having a thickness of 0.5 .mu.m. In this manner, two silicon wafers were prepared. Then, on one wafer, an. . .

By **coating** the composition of the present invention, the mechanical properties in a high temperature region will be remarkably improved as compared with usual resins having low dielectric constants, and it is possible to obtain a uniform **coating** film, and the reliability in the case exposed at high temperatures, will be substantially improved. Especially when it is applied to a **semiconductor** device or a multi-layered circuit board, it is possible to accomplish reduction of the time of signal propagation

delay

by. . .

AN 864926 EUROPATFULL ED 19980927 EW 199838 FS OS
TIENT PHOTSENSITIVE RESIN COMPOSITION, AND COATING FILM, RESIST INK, RESIST,
TIDE SOLDER RESIST AND PRINTED CIRCUIT BOARD EACH PRODUCED THEREFROM.
PHOTOEMPFFINDLICHE HARZZUSAMMENSETZUNG UND BESCHICHTUNGSFILM,
RESISTTINTE, RESIST, LOETSTOPPRESIST UND GEDRUCKTE LEITERPLATTE, DIE
AUS DER ZUSAMMENSETZUNG HERGESTELLT WERDEN.
TIFR COMPOSITION DE RESINE PHOTSENSIBLE ET COUCHE MINCE DE REVETEMENT,
ENCRE RESIST, RESIST DE SOUDURE ET PLAQUETTE A CIRCUITS IMPRIMES REALISES
AVEC CETTE COMPOSITION.
IN HASHIMOTO, Soichi, Goo Chemical Industries Co. Ltd, 58, Ijiri
Iseda-cho,
Uji-shi, Kyoto 611, JP;
SUZUKI, Fumito, Goo Chemical Industries Co., Ltd., 58, Ijiri Iseda-cho,
Uji-shi, Kyoto 611, JP
PA Goo Chemical Industries Co.,Ltd., 58, Ijiri Iseda-cho, Uji-shi, Kyoto
611, JP
PAN 2206910
AG Brooks, Nigel Samuel, Hill Hampton East Meon, Petersfield Hampshire
GU32 1QN, GB
AGN 47731
OS ESP1998063 EP 0864926 A1 980916
SO Wila-EPZ-1998-H38-T2a
DT Patent
LA Anmeldung in Japanisch; Veroeffentlichung in Englisch;
Verfahren in Englisch
DS R AT; R CH; R DE; R FR; R GB; R IT; R LI
PIT EPAL EUROPAEISCHE PATENTANMELDUNG (Internationale Anmeldung)
PI EP 864926 A1 19980916
OD 19980916
AI EP 1995-942626 19950313
RLI WO 95-JP414 950313 INTAKZ
WO 9628764 960919 INTPNR
DETDEN. . . such as toluene, xylene, etc.; acetates such as ethyl acetate,
butyl acetate, cellosolve acetate, butylcellosolve acetate,
butylcarbitol acetate, propylene glycol **monomethyl**
ether acetate, etc.; dialkylene glycol ethers, etc. These
organic solvents can be used singly or as their mixtures.
The . . . 50 to 150.degree.C, especially preferably from at 60 to
120.degree.C, by adding a thermal polymerization inhibitor such as
hydroquinone, hydroquinone **monomethyl ether** or the
like, a tertiary amine such as benzyldimethylamine, triethylamine or
the like, a quaternary ammonium salt such as trimethylbenzylammonium. .
The . . . dipropylene glycol methyl ether, etc.; acetates such as
ethyl acetate, butyl acetate, cellosolve acetate, butylcellosolve
acetate, butylcarbitol acetate, propylene glycol **monomethyl**
ether acetate, etc.; dialkylene glycol ethers, etc.
In . . . such as silicones, acrylate copolymers, fluorine-containing
surfactants, etc.; adhesiveness improving agents such as silane
coupling agents; thixotropic agents such as **aerogel**, etc.;
polymerization inhibitors such as hydroquinone, hydroquinone
monomethyl ether, pyrogallol, tert-butyl catechol,
phenothiazine, etc.; other various additives such as anti-halation
agents, flame retardants, de-foaming agents, antioxidants, etc.; and
also. . .

L12 ANSWER 85 OF 87 EUROPATFULL COPYRIGHT 1999 WILA

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 822545 EUROPATFULL ED 19980215 EW 199806 FS OS
TIEN Optical component and spirobiindan polymer therefor.
TIDE Optisches Bauelement und Spirobiindan-Polymer dazu.
TIFR Composant optique et polymere de spirobiindane pour cette utilisation.
IN Otsuji, Atsuo, 2882-4-21, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Takuma, Keisuke, 1172-3-402, Kamikuratomachi, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Suzuki, Rihoko, 8-11-A-25, Isogo, Isogo-ku, Yokohama-shi, Kanagawa, JP;
Urakami, Tatsuhiro, 3-42-7, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Motoshima, Toshihiro, 2882-2-49, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Yamashita, Watura, Mitsui Kagaku Apaat 522, Hirabarumachi, Omuta-shi, Fukuoka, JP;
Yoshimura, Tomomi, 1959-128, Shinyoshidacho, Kohoko-ku, Yokohama-shi, Kanagawa, JP;
Shibuya, Atsushi, 3-42-7-516, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Sakata, Yoshihiro, 4-5-45-214, Dai, Kamakura-shi, Kanagawa, JP;
Oikawa, Hideaki, 3-42-7-212, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Ohta, Masahiro, 2-6-41, Komachi, Kamakura-shi, Kanagawa, JP;
Ajioka, Masanobu, 1172-3-202, Kamikuratomachi, Totsuka-ku, Yokohama-shi, Kanagawa, JP;
Takagi, Masatoshi, 2882-3-28, Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa, JP;
Karasawa, Akio, 3-42-7, Hirado, Totsuka-ku, Yokohama-shi, Kanagawa, JP
PA MITSUI TOATSU CHEMICALS, INCORPORATED, 2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, JP
PAN 204177
AG Stuart, Ian Alexander et al, MEWBURN ELLIS York House 23 Kingsway, London WC2B 6HP, GB
AGN 50492
OS ESP1998008 EP 0822545 A2 980204
SO Wila-EPZ-1998-H06-T2a
DT Patent
LA Anmeldung in Englisch; Veroeffentlichung in Englisch
DS R AT; R BE; R CH; R DE; R DK; R ES; R FI; R FR; R GB; R GR; R IE; R IT; R LI; R LU; R MC; R NL; R PT; R SE
PIT EPA2 EUROPAEISCHE PATENTANMELDUNG
PI EP 822545 A2 19980204
OD 19980204
AI EP 1997-305763 19970731
PRAI JP 1996-201825 19960731
JP 1996-204614 19960802
JP 1996-204615 19960802
JP 1996-331831 19961212
JP 1996-331832 19961212
JP 1996-331833 19961212

DETDEN. . . agent are as follows. The monovalent hydroxy aliphatic or aromatic compounds include methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol **monomethyl ether**, cyclohexanol, benzyl alcohol, allyl alcohol, phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, 4-phenylphenol, 4-cyclohexylphenol, 4-n-octylphenol, 4-isooctylphenol, 4-nonylphenol, 4-methoxyphenol, 4-n-hexyloxyphenol, . . .
In . . . necessary, there may be added inorganic fillers such as talc, alumina, barium sulfate and magnesium oxide; thixotropy agents

such as **aerogel**; melamine resins such as hexamethoxy melamine and hexabutoxy melamine; leveling agents such as silicone, fluorinated polymers and acrylate copolymers; color. . . .

Specific . . . regulating agent are as follows. Monovalent hydroxy aliphatic or aromatic compounds include methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol **monomethyl ether**, cyclohexanol, benzyl alcohol, allyl alcohol, phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, 4-phenylphenol, 4-cyclohexylphenol, 4-n-octylphenol, 4-isooctylphenol, 4-nonylphenol, 4-methoxyphenol, 4-n-hexyloxyphenol, . . .

Examples . . . such a molecular-weight regulating agent include monovalent aliphatic hydroxy compounds such as methanol, ethanol, butanol, octanol, lauryl alcohol, methoxyethanol, propyleneglycol **monomethyl ether**, cyclohexanol, benzyl alcohol and allyl alcohol;

aromatic hydroxy compounds such as phenol, 4-tert-butylphenol, 2-cresol, 3-cresol, 4-cresol, 2-ethylphenol, 4-ethylphenol, 4-cumylphenol, . . .

In . . . there may be added inorganic fillers such as talc, silica, alumina, barium sulfate and magnesium oxide; thixotropy agents such as **aerogel**; melamine resins such as hexamethoxy melamine and hexabutoxy melamine; leveling agents such as silicone, fluorinated polymers and acrylate copolymers; color. . . .

L12 ANSWER 1 OF 87 USPTAFULL
 AN 1998:162230 USPTAFULL
 TI Photosensitive resin compositions, cured films thereof, and circuit boards
 IN Yanagawa, Makoto, Saitama, Japan
 Tachibana, Rinzo, Saitama, Japan
 Yamamoto, Hiroshi, Saitama, Japan
 Ishikawa, Tetsuji, Kanagawa, Japan
 Kurokawa, Tetsuo, Kanagawa, Japan
 Ishida, Kohichi, Kanagawa, Japan
 PA Tamura Kaken Co., Ltd, Japan (non-U.S. corporation)
 PI US 5853957 19981229
 AI US 1996-646464 19960508 (8)
 PRAI JP 1995-132618 19950508
 DT Utility
 EXNAM Primary Examiner: Hamilton, Cynthia
 LREP King and Schickli
 CLMN Number of Claims: 12
 ECL Exemplary Claim: 1,3,4,5,6
 DRWN No Drawings
 LN.CNT 1428
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.
 SUMM . . . compounds, acrylate copolymers, and fluorine surfactants; an adhesion imparting agent such as silane coupling agents; a thixotropic agent such as **aerogels**; a polymerization inhibitor such as hydroquinone, hydroquinone **monomethyl ether**, pyrogallol, t-butyl catechol, and phenothiazine; a dispersion stabilizer
 such as various surfactants, and high-molecular dispersants; and various additives such as. . . .

L12 ANSWER 2 OF 87 USPTAFULL
 AN 1998:54976 USPTAFULL
 TI Stable particulate dispersions
 IN Okoroafor, Michael O., Export, PA, United States
 McDonald, William H., Cranberry Township, PA, United States
 Wang, Alan E., Hoffman Estates, IL, United States
 PA BASF Corporation, Mount Olive, NJ, United States (U.S. corporation)
 PI US 5753735 19980519

AI US 1997-876945 19970616 (8)
RLI Division of Ser. No. US 1997-795736, filed on 5 Feb 1997, now patented,
Pat. No. US 5691392
DT Utility
EXNAM Primary Examiner: Foelak, Morton
CLMN Number of Claims: 19
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 778

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . formulations to facilitate foam formation. See, for example,
U.S. Pat. No. 4,751,251. It has been proposed that silica, e.g., silica
aerogel, be added to rigid polyurethane foam formulations to
enhance the insulating properties of such foams when fluorocarbon
blowing agents are. . . .

SUMM . . . "particulate dispersion" is meant a dispersion of a solid
particulate material(s), e.g., a silica such as precipitated silica or
silica **aerogel**, in a liquid medium (continuous phase) wherein
the particulate material(s) does not agglomerate and/or settle within a
period of three. . . .

SUMM . . . include, but are not limited to: propylene carbonate;
2-methoxyethyl ether; dipropylene glycol, methyl ether; triethylene
glycol, dimethyl ether; triethylene glycol, **monomethyl**
ether; tripropylene glycol, **monomethyl ether**
; methyl-2,5-dihydro-2,5-methoxy-2-furancarboxylate;
1-methoxy-2-methylpropylene oxide; 2-methoxy ethyl acetoacetate;
diethylene glycol, **monomethyl ether**,
2-methoxy-1,3-dioxolane; methoxyacetone; methoxyacetaldehyde,
dimethylacetal; methoxyacetaldehyde diethyl acetal; 2,5-dimethoxy
tetrahydrofuran; 2,5-dimethoxy-3-tetrahydrofurano carboxaldehyde;
2,2-dimethoxy propane; 1,2-dimethoxy propane and dimethoxy methane.
Examples of. . . .

SUMM . . . such as calcium carbonate; metal oxides-such as iron oxide;
talc; mica; and silicas such as precipitated silicas, fumed silicas,
silica **aerogels**, hydrophobic silicas, and hydrophilic silicas.

SUMM . . . rigid polyurethane foams, the preferred particulate material
is

silica. Classes of silica that may be used include, for example, silica
aerogels, fumed silicas, precipitated silicas, and in particular
hydrophobic and hydrophilic precipitated silicas. Preferred particulate
materials may be selected from the group consisting of fumed silica,
precipitated silica, silica **aerogel**, and mixtures of such
silicas.

CLM What is claimed is:

. . . composition of claim 1 wherein said particulate material is selected
from the group consisting of fumed silica, precipitated silica, silica
aerogel, and mixtures of such silicas.

. . . method of claim 11 wherein said particulate material is selected
from

the group consisting of fumed silica, precipitated silica, silica
aerogel, and mixtures of such silicas; and said nonionic organic
surfactant is selected from at least one member selected from of. . . .

L12 ANSWER 3 OF 87 USPATFULL

AN 97:109948 USPATFULL

TI Stable particulate dispersions

IN Okoroafor, Michael O., Export, PA, United States

McDonald, William H., Cranberry Township, PA, United States

Wang, Alan E., Hoffman Estates, IL, United States

PA PPG Industries, Inc., Pittsburgh, PA, United States (U.S. corporation)

PI US 5691392 19971125

AI US 1997-795736 19970205 (8)

DT Utility

EXNAM Primary Examiner: Foelak, Morton

LREP Stein, Irwin M.
CLMN Number of Claims: 11
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 734

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . formulations to facilitate foam formation. See, for example, U.S. Pat. No. 4,751,251. It has been proposed that silica, e.g., silica **aerogel**, be added to rigid polyurethane foam formulations to enhance the insulating properties of such foams when fluorocarbon blowing agents are. . . .

SUMM . . . particulate dispersion" is meant a dispersion of a solid particulate material(s), e.g., a silica such as precipitated silica or silica **aerogel**, in a liquid medium (continuous phase) wherein the particulate material(s) does not agglomerate and/or settle within a period of three. . . .

SUMM . . . include, but are not limited to: propylene carbonate; 2-methoxyethyl ether; dipropylene glycol, methyl ether; triethylene glycol, dimethyl ether; triethylene glycol, **monomethyl ether**; tripropylene glycol, **monomethyl ether**; methyl-2,5-dihydro-2,5-methoxy-2-furancarboxylate; 1-methoxy-2-methylpropylene oxide; 2-methoxy ethyl acetoacetate; diethylene glycol, **monomethyl ether**, 2-methoxy-1,3-dioxolane; methoxyacetone; methoxyacetaldehyde, dimethylacetal; methoxyacetaldehyde diethyl acetal; 2,5-dimethoxy tetrahydrofuran; 2,5-dimethoxy-3-tetrahydrofurano carboxaldehyde; 2,2-dimethoxy propane; 1,2-dimethoxy propane and dimethoxy methane. Examples of. . . .

SUMM . . . as calcium carbonate; metal oxides such as iron oxide; talc; mica; and silicas such as precipitated silicas, fumed silicas, silica **aerogels**, hydrophobic silicas, and hydrophilic silicas.

SUMM . . . rigid polyurethane foams, the preferred particulate material is silica. Classes of silica that may be used include, for example, silica **aerogels**, fumed silicas, precipitated silicas, and in particular hydrophobic and hydrophilic precipitated silicas. Preferred particulate materials may be selected from the group consisting of fumed silica, precipitated silica, silica **aerogel**, and mixtures of such silicas.

CLM What is claimed is:

. . . composition of claim 1 wherein said particulate material is selected from the group consisting of fumed silica, precipitated silica, silica **aerogel**, and mixtures of such silicas.

L12 ANSWER 5 OF 87 USPATFULL

AN 97:49442 USPATFULL

TI Storage-stable advanced polymaleimide compositions

IN Chin, Benjamin G., Croton-on-Hudson, NY, United States

Tietze, Roger, Baldwin, NY, United States

PA Ciba-Geigy Corporation, Tarrytown, NY, United States (U.S. corporation)

PI US 5637387 19970610

AI US 1995-462438 19950602 (8)

RLI Continuation of Ser. No. US 1994-241216, filed on 10 May 1994, now abandoned which is a continuation-in-part of Ser. No. US 1993-117886, filed on 7 Sep 1993, now abandoned which is a continuation of Ser. No. US 1991-709906, filed on 3 Jun 1991, now abandoned

DT Utility

EXNAM Primary Examiner: Reddick, Judy M.

LREP Kovalski, Michele A.

CLMN Number of Claims: 24

ECL Exemplary Claim: 1

DRWN No Drawings

LN.CNT 812

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . such as acetone, methyl ethyl ketone and methyl isobutyl ketone; glycol ethers and glycol ether acetates such as propylene glycol

monomethyl ether, propylene glycol methyl ether acetate, ethylene glycol methyl ether, ethylene glycol ethyl ether and glycol ethyl ether acetate; hydrocarbons such. . . 1:1) being of particular interest. Most preferably, methyl ethyl ketone or a mixture of methyl ethyl ketone and propylene glycol **monomethyl ether** is used. Blends of ketones with certain higher boiling solvents are also applicable.

SUMM . . . glass fibers, boron fibers, carbon fibers, cellulose, polyethylene powder, polypropylene powder, mica, asbestos, quartz powder, gypsum, antimony trioxide, bentones, silica **aerogel** ("aerosil"), lithopone, barite, titanium dioxide, carbon black, graphite, iron powder. It is also possible to add other usual additives, for. . .

DETD

Formulation	Parts by Weight
-------------	-----------------

Bismaleimidodiphenylmethane	31.9
Diallyl Bisphenol A	27.3
Tripropylamine	0.38
Phenothiazine	1.0
Methyl Ethyl Ketone	19.7
Propylene Glycol Monomethyl Ether	19.7

DETD

Formulation	Parts by Weight
-------------	-----------------

Bismaleimidodiphenylmethane	31.9
Diallyl Bisphenol A	27.3
Tripropylamine	0.38
Methyl Ethyl Ketone	20.0
Propylene Glycol Monomethyl Ether	20.0

DETD

Formulation	Parts by Weight
-------------	-----------------

Bismaleimidodiphenylmethane	32.0
Diallyl Bisphenol A	27.5
Tripropylamine	0.38
Phenothiazine	0.40
Methylethylketone	19.8
Propylene Glycol Monomethyl Ether	19.8

CLM What is claimed is:

. . . 12. A storage-stable prepolymer polymaleimide composition according to claim 10, wherein a mixture of methyl ethyl ketone and propylene glycol **monomethyl ether** is the solvent.